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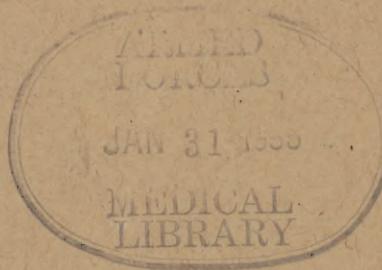
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HYDROGEN PEROXIDE

PRODUCTION THROUGH 2-ETHYL ANTHRAQUINONE



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COMBINED INTELLIGENCE OBJECTIVES

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HYDROGEN PEROXIDE, PRODUCTION
OF THROUGH 2-ETHYL ANTHRAQUINONE

PAGE

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Method to produce

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April 1945

THURSDAY

CIOS Item Number 22
Miscellaneous Chemicals

COMBINED INTELLIGENCE OBJECTIVES SUB-COMMITTEE
G-2 Division, SHAEF (Rear) APO 413

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SUMMARY

The interrogation of Dr. George Pfleiderer of the Ludwigshaven Plant of I. G. Farben Industrie, disclosed the production of Hydrogen Peroxide on a small plant scale through the use of easily oxidizable organic materials, specifically 2 Ethylanthraguinone. This is probably the only new method of hydrogen peroxide production in Germany. Commander P. Talmey, USNR., departed 6 April for the United States carrying micro-film of the available literature which should be used in conjunction with this report.

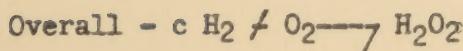
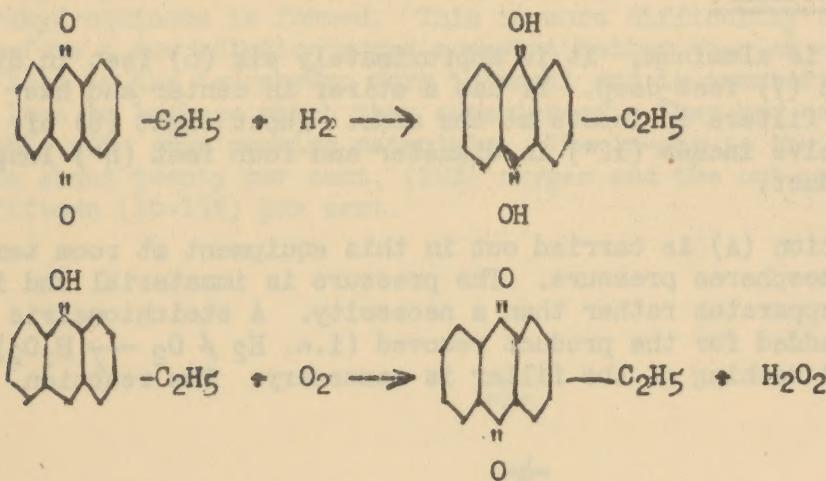
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1. Introduction.

Interrogation of Dr. George PFLEIDERER of Ludwigshaven Plant of I. G. Farben Industrie.

The conventional methods of hydrogen peroxide production are all electro chemical reactions involving the oxidation of solutions of sulfuric acid or ammonium sulfate. It has been known that reactions involving the oxidation of easily oxidizable organic materials and the extraction of the resulting peroxide with water could be used; however, many factors limited the interest in these processes to laboratory investigation. The process described here as invented by Dr. George Pfleiderer and Dr. Hans-Joachim Riedl had been operated successfully at Ludwigshaven for several months before it was bombed out. The process is covered in general by German patent No. 671318 issued 14 October 1941, a copy of which is available. The value of this disclosure is that the feasibility of large scale production of peroxide is relatively simple and inexpensive equipment by non-electrolytic methods has been proven. The plant described is for the daily production of one metric ton of H_2O_2 calculated on 100% H_2O_2 basis. Plans had been drawn up for the building of an eleven ton daily plant, but these were not completed. Some of these drawings and calculations are available to us, but the bulk were shipped farther into Germany. It was Dr. Pfleiderer's opinion that no other new method of peroxide production is being used in Germany. The German schematic drawign of this process was found in Heidelberg after the interrogation of Dr. Pfleiderer and the explanation of some of the units is not known.

2. Chemistry of the Process.



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3. Notes on the Process.

In the one (1) ton/day unit the total working solution is fifteen (15) cubic meters of which one-quarter ($\frac{1}{4}$) is in the reductor, one-quarter ($\frac{1}{4}$) in the oxidizer and one-half ($\frac{1}{2}$) in the other vessels. The total time for circulation is two (2) hours. The main difficulty is reaction (A). This is carried out by passing hydrogen through the quinone in a solution of fifty per cent, (50%) thiophene free benzene and fifty percent, (50%) cyclohexanol in the presence of Raney nickel. It is preferable to use other higher aliphatic alcohols (C₇- C₁₁) if possible. Raney nickel is a commercially available catalyst made by alloying nickel and aluminum, dissolving out the aluminum with caustic and powdering the remaining nickel. Referring to the flow diagram by Eric H. REICHL, which was conceived on the basis of Dr. Pfleiderer's description:

Step 1 (Precontactor)?

(a) Use: Converts remaining H₂O₂ ($\frac{1}{100}$ N) with hydroquinone. $\frac{1}{10}$ of the total hydroquinone is circulated through the Precontactor. This is an excess, but free H₂O₂ poisons the nickel catalyst.

(b) Construction Material - Aluminum: Contains one (1) cubic meter of catalyst, - a porous clay carrier containing metallic nickel and silver. These are formed by the co-precipitation from the salts and the subsequent reduction to the metal. The life of this catalyst was not reached in several months of production. We did not determine the amount of metals used. The solution leaving the precontactor contains one hundred (100) g. of the quinone perliter.

Step 2 - Reducer:

(a) This is aluminum. It is approximately six (6) feet in diameter and seven (7) feet deep. It has a stirrer in center and has porous ceramic filters in insets at the side. About eight (8) of these tubes twelve inches (12") in diameter and four feet (4') long filter the product.

(b) Reaction (A) is carried out in this equipment at room temperature and 1-2 atmospheres pressure. The pressure is immaterial and is a result of the apparatus rather than a necessity. A stoichiometric amount of H₂ is added for the product removed (i.e. H₂ + O₂ → H₂O₂). Occasional back washing of the filter is necessary. The reaction

Step 2 - Reducer (b) (Cont'd.)

vessel as seen had some cooling coils around the bottom. Only one half of the total quinone is reduced to hydroquinone in the reduction step. This is done purposefully because the combined presence of hydroquinone and quinone causes formations of quinhydrone which increases the solubility of the hydroquinone in the solution.

Step 3 - After Filter:

(a) A bag type filter is used. The cloths rarely need changing. A filter press had previously been used, but was abandoned. They had some trouble here with pressure drop.

Step 4 - Cooler:

(a) A water cooler is used. Roughly one-half ($\frac{1}{2}$) the heat of the overall reaction is removed.

Step 5 - Oxidizer:

(a) Material - Enamelled Iron. It was stated that aluminum material could not be used wherever peroxide and hydroquinone solution were copresent because of corrosion.

(b) The heat pick up on the oxidizer is 7-8° C from roughly 30° to 37°. The entire mixing is done by dispersing the gas through a porous plate. The N₂ is recycled to eliminate loss of benzene vapor in N₂ effluent. Oxygen is added to the cycle. The oxydation is essentially complete. No hydroquinone is present in the exit. However, a slow hydrogenation of hydroquinone takes place in the reducer and tetrahydroquinone is formed. This is more difficultly oxidized and therefore a new solution works somewhat better than an old solution. The loss to the tetrahydro form is small and is immaterial compared to the loss to leakage which they experienced. They had considerable trouble with pump packing materials. The in-gas to the oxidizer contains about twenty per cent, (20%) oxygen and the out-gas contains ten to fifteen (10-15%) per cent.

Step 6 - Water Wash:

(a) Material - Enamelled Iron. Iron free water enters at top of reactor counter current to benzene solutions. Twenty per cent. (20%) H₂O₂ solution is drawn off the bottom. The product can be stabilized and sold as such or further concentrated. The quinone solution is taken off the top. It contains (.1 - .3%) water (saturated) and 1/100 N H₂O₂. The water is removed by sending through thirty-three percent. (33%) K₂CO₃ solution. This solution is maintained at strength by addition of fifty per cent. (50%) K₂CO₃ solution. The wash tower contains Raschig rings.

Step 7 - After Cooler:

(a) Approximately one-half ($\frac{1}{2}$) total heat of reaction is taken off here.

Step 8 - Absorption Filters:

(a) One (1) cubic meter of activated alumina for removal of organic impurities. The life of this absorber was never reached.

Step 9:

(a) The product taken out the bottom of wash tower contains twenty per cent. (20%) H₂O₂ at a PH of approximately 6.0 plus impurities consisting of benzene, some alcohols carried over and traces of water soluble acids. The tests run on the product are for total carbon which runs (.05 - .1%). If solution is allowed to stand in this condition, the acids increase. This solution is stabilized with twenty (20) mg. Na₂SnO₃/l and thirty (30) mg. NH₄NO₃/l is added presumably to inhibit aluminum corrosion. It was Pfleiderer's contention that stannate is better for this product, but that Phosphoric acid was better for the product of other processes.

(b) If it is desirable to concentrate the product, a two stage distillation is used. This is explained in the report entitled Renalldistillation of 16 August 1944. Sixty per cent. (60%) H₂O₂ is taken off the first stage and eighty to eighty-five per cent. (80 - 85%) off the second. A vacuum of forty to fifty (40 - 50) mm. Hg is maintained. H₂O and some benzene is taken off the top of the first column and H₂O is taken off the top of the second column.

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4. Shipping Materials.

(a) Aluminum containers are used. Other materials were tried with a plastic covering but because of the plastic's permeability, the H₂O₂ seeped through the covering, decomposed on the metal and caused blisters.

(b) Gasketing and Construction Plastics:

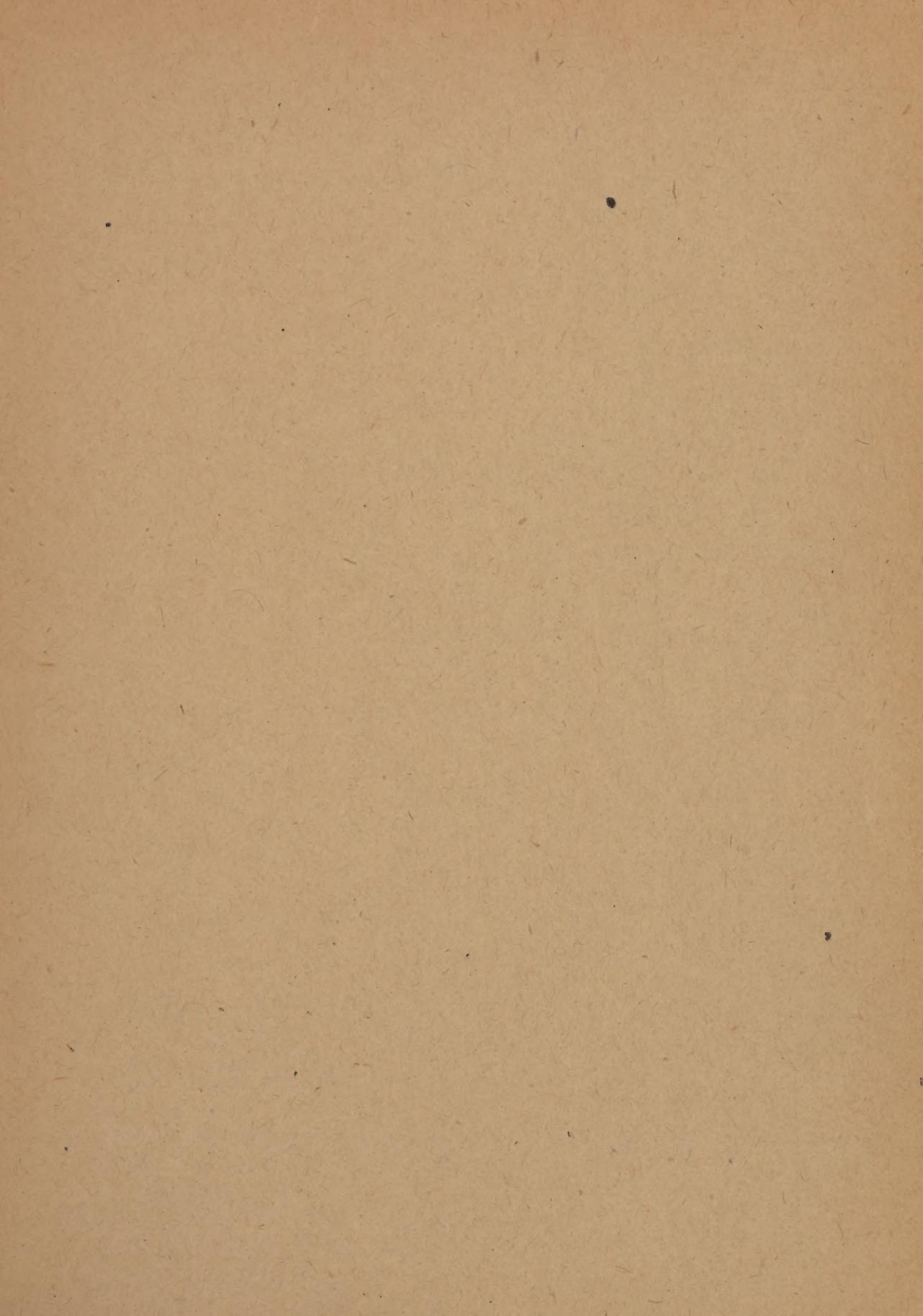
- (1) Vinol - Made by Walcher & Company, a polyvinyl chloride containing fifty percent (50%) Cl₂.
- (2) Igelit - An I. G. Product same as above.
- (3) Vinidur - Same as above without softener.

5. Available Literature.

1. Patent - Verfahren zur Herstellung Von Wasserstoffsuperoxyd Reichspatentant No. 671318 to Dr. Hans Joachim Reidl and Dr. George Pfleiderer issued 14 October 1941.
2. Herstellung Von Wasserstoffsuperoxyd und alkaliperoxyden über autoxydable organische verbindungen 1936.
3. Verfahren zur Darstellung Von Wasserstoffsuperoxyd 1935.
4. Verfahren zur Herstellung Von Peroxyden 1937.
5. Verfahren zur Herstellung Von Peroxyden insbesondere Wasserstoffsuperoxyd 1938.
6. Schematic drawing of Process Pe 002 N4844-8.
7. Flow chart Pe 001 N 4217-16 / some calculations.
8. Renaldestillation. 16 August 1944.
9. Wasserstoffsuperoxyd 5 January 1942.
10. Protokoll: Renal-analage 1943.
11. Actilkohle - analage zur wiedergewinnung von Benzol - a letter 8-30-43.
12. An unlabeled drawing of Pfleiderer Process.
13. A Schematic drawing of Pfleiderer Process by E. H. Reichl.
14. Arbeiten zur Renaldistillation - a report on methods of distillation.
15. Loose papers containing calculations on distillation.

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